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A CONE TEN SANITARY WARE GLAZE OF THE FRITTED LEADLESS TYPE

BY

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THESIS

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I - INTRODUCTION

Sanitary ware glazes constitute a very important type of glaze in the ceramic industry of today. There are several kinds of these glazes, the one which is used to a great extent in the United States being the Bristol type with the addition of lead.[1] Other manufacturers are using the same vitrified white glaze on their sanitary ware as they use on their vitrified china ware.[3]

Of recent years the tendency among the more progressive manufacturers of sanitary ware has been to eliminate the use of lead in their glazes because of its injurious effects upon the men working in the glaze room. In order to replace the lead glazes, however, the leadless glazes must have equally desirable qualities, at least as regards gloss, acid resistance, heat range, working properties, etc. as the lead glazes. Sanitary ware glazes are usually burned at temperatures ranging from cone four to cone nine, depending on the type of glaze used.

'In general two types of body are in use. For the very heavy articles such as bath tubs, sinks, etc. a so called fireclay body is used. For the lighter goods such as small lavatories, closets, and tanks, it is customary to use a vitreous white ware composition!'[2]

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References -

1. 'Fritted Leadless Glazes for Sanitary Ware' by C. W. Parmelee and G. A. Williams, T.A.C.S., vol. 18, page 812

2. Clay Products Cyclopedia and Catalog

3. The Clay Worker, Vols. 83 and 84

II

REVIEW OF LITERATURE

After examining all the available sources of information only three references were found containing information which would aid materially in solving the problem. The most important andthe one which was used greatly in planning the thesis was an investigation conducted by C. W. Parmelee and G. A. Williams and published in the Transactions of the American Society, vol. eighteen, as 'Fritted Leadless Glazes for Sanitary Ware'. The summary of their results which are for cone seven is as follows; 'the silica content giving the best results as to gloss was five equivalents. The amount of alumina to be recommended lies at either 0.50 or 0.60 equivalents for glossy glazes, although less than this may be used with 0.50 equivalents of boric oxide present. With series having three and four equivalents of silica, 0.70 equivalents of alumina gives matte or immature glazes with all contents of boric oxide. The most favorable B_2O_3 content is 0.50 equivalents. The best range of RO members was within the limits

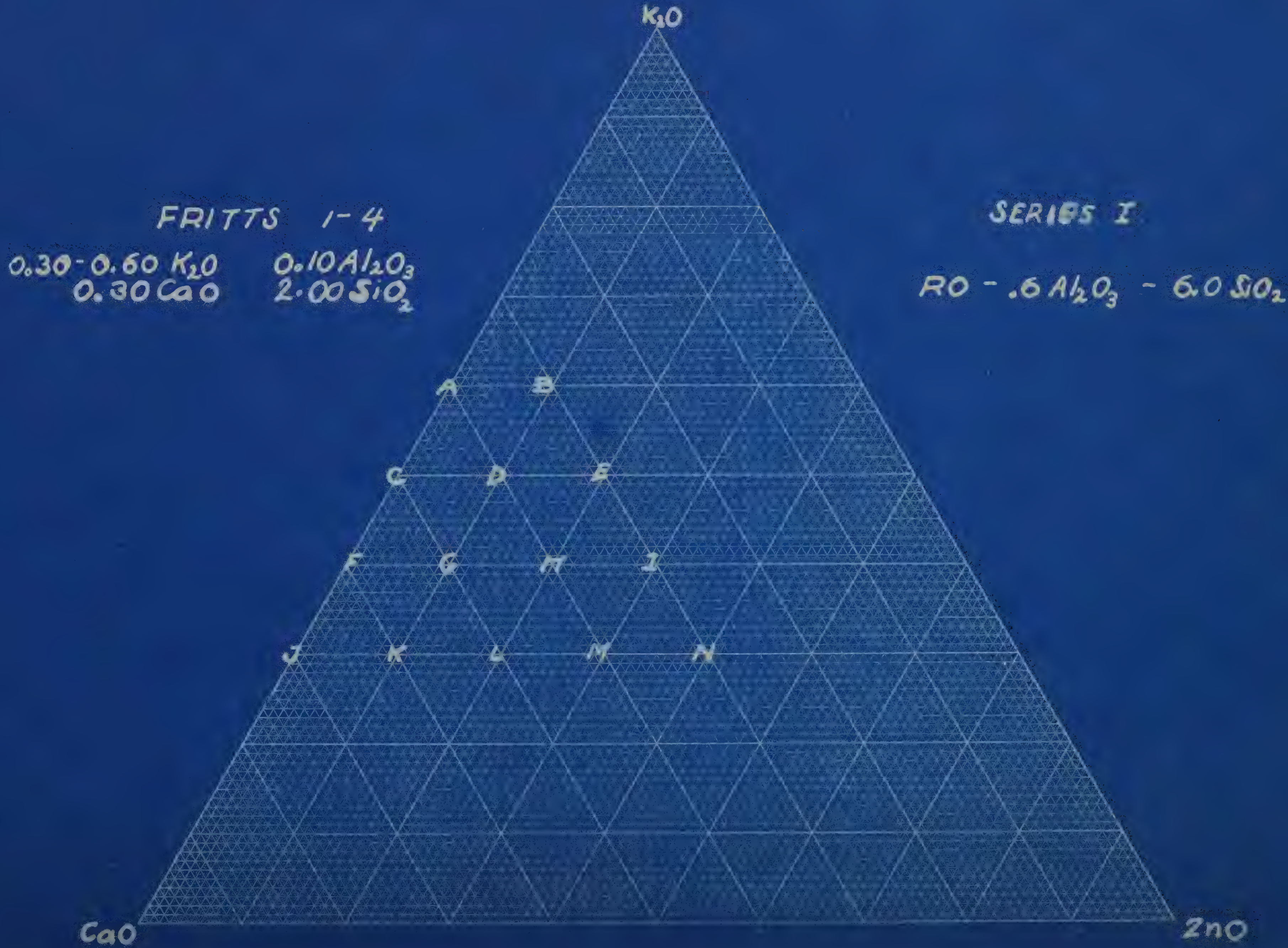
0.40 -- 0.60 K_2O

0.00 -- 0.30 ZnO

0.40 -- 0.60 CaO

The substitution of pearl ash in place of potassium nitrate did not affect the results appreciably, and substitution of Na_2O for K_2O merely extended the area of good glazes.

FIGURE I



K2O
FRITTS 1-4
0.30-0.60 K2O 0.10 Al2O3
0.30 CaO 2.00 SiO2
SERIES I
RO - .6 Al2O3 - 6.0 SiO2
A B
C D E
F G H I
J K L M N
CaO
ZnO

III. EXPERIMENTAL WORK

It was decided to carry out this investigation in the same manner as a typical glaze problem, that is, cover the field of possible RO composition, keeping the Al_2O_3, B_2O_3 and SiO_2 constant; then choosing the best of these RO groups, vary the Al_2O_3, B_2O_3 and SiO_2, In this manner a large part of the field of possible good glazes could be covered without undue labor.

SERIES I

In this series the members of the RO groups were varied as shown in Figure I, the ZnO varying from 0.00 - 0.40 equivalents, the K_2O from 0.30 - 0.60 equivalents, and the CaO from 0.30 - 0.70 equivalents. The alumina and silica remained constant at 0.60 and 6.00 equivalents respectively. In this series four fritts were used, their compositions differing only in the amount of K_2O present. All the K_2O was added in the firtts. The composition of the fritts are shown in Figure I.

SERIES II.

This series differs from series I and II only by the addition pf 0.50 equivalents of boric oxide. The composition of the fritt is shown on Figure II.

SERIES III.

Three of the best glazes from series I and II were chosen and the boric oxide varied from o.4o - 0.60 equivalents, and the

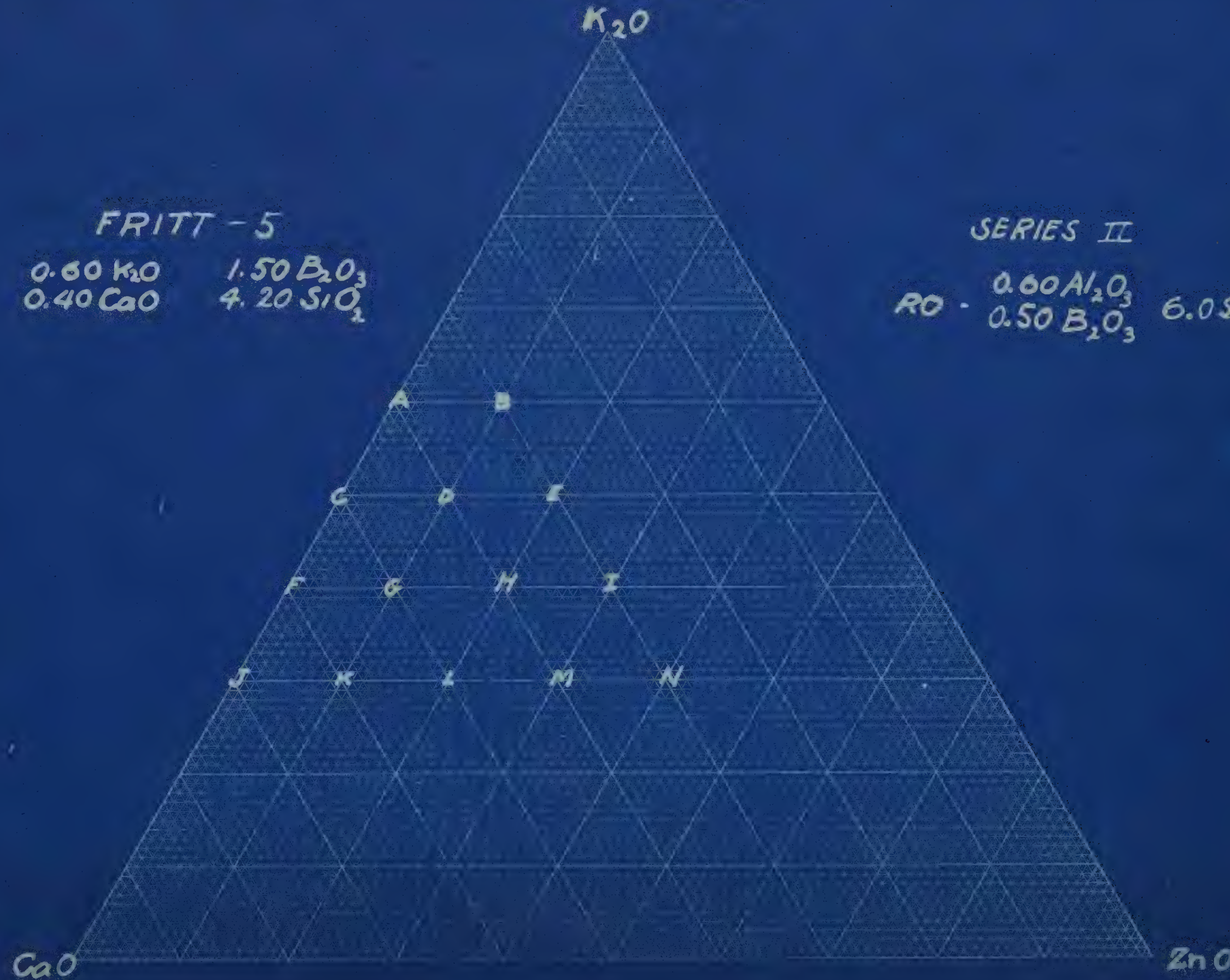
FIGURE II

FRITT - 5

0.60 K_2O 1.50 B_2O_3
0.40 CaO 4.20 SiO_2

SERIES II

RO - 0.60 Al_2O_3 0.50 B_2O_3 6.0 SiO_2



Al_2O_3 varied from 0.5 - 0.7 equivalents; the silica remaining constant at 6.00 equivalents.

SERIES IV

This series differs only from series III in that the silica remains constant at seven equivalents instead of six equivalents. The same fritt was used for both series III and series IV. Its composition is as follows :-

0.60 -- K_2O	1.20 -- B_2O_3
0.40 -- CaO	2.6 -- SiO_2

In order to approach actual conditions as closely as possible the glazes were burned on trial pieces made up of a typical sanitary ware body.#

This body was prepared by blunging the materials for about three hours, then passing it through a 120 mesh screen to remove any impurities as coal, etc.. After removing the surplus water by drying the body in a plaster bat, it was thoroughly wedged and then made into bars by pressing by hand in a steel mold. These trial pieces were then burned in a gas-fired kiln to cone 8½ - 9. The composition of the body is as follows:

Buckingham Feldspar ----	16
Quartz Flint ----	32
Tenn. #5 Ball Clay ----	12
H&G Eng. China Clay ----	25
Florida Clay ----	15

The raw materials used in making up the glazes were assumed to be pure, and are given together with their formulas:

#The composition of this body was suggested by Prof. C. W. Parmelee

1. Zinc Oxide - ZnO
2. Boric Acid - $B_2O_3 \cdot 3\ H_2O$
3. Pearl Ash - K_2CO_3
4. Commercial Whiting - $CaCO_3$
5. Florida Clay - used as a flot

   assumed to have formula - $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

All fritting was done by the drop firtt method, the fritts then being ground dry to pass 150 mesh, and the glazes subsequently passed through 120 mesh.

Following is a summary of the firtts used:

Number	1	2	3	4	5	6
Used in Series	I	I	I	I	II	III & IV
K_2O	0.60	0.50	0.40	0.30	0.60	0.60
CaO	0.30	0.30	0.30	0.30	0.40	0.40
B_2O_3	---	---	---	---	1.50	1.50
Al_2O_3	0.10	0.10	0.10	0.10	---	---
SiO_2	2.00	2.00	2.00	2.00	2.60	2.60

The raw materials used in the fritts are as follows:

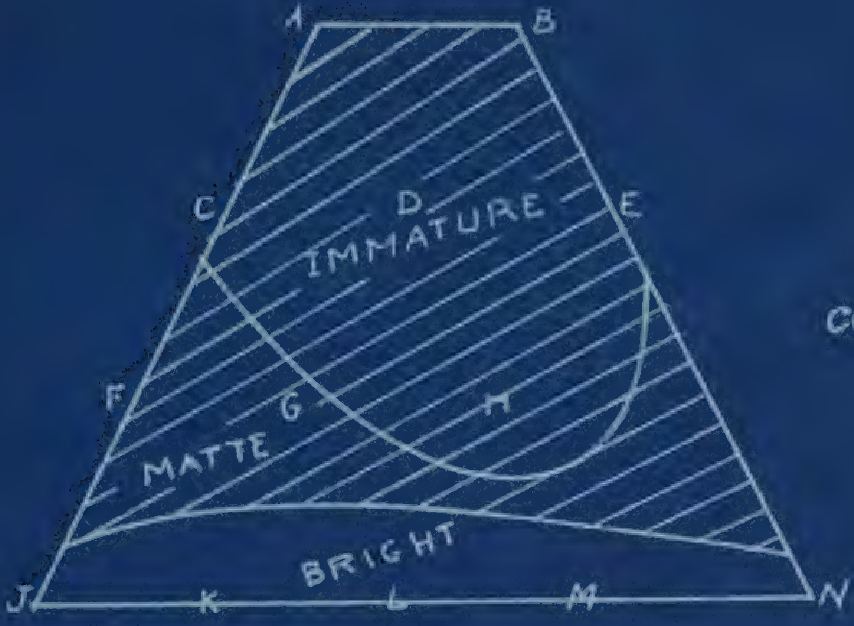
K_2O was added as Pearl Ash
CaO was added as Whiting
B_2O_3 was added as Boric Acid
Al_2O_3 was added as Florida Clay
SiO_2 was added as clay and as Quartz Flint

Actual composition of fritts by weights:

Number	I	II	III	IV	V	VI
Pearl Ash	83	69	55	41	83	83
Commercial Whiting	30	30	30	30	40	40
Boric Acid	--	--	--	--	185	185
Florida Clay	26	26	26	26	--	--
Quartz Flint	108	108	108	108	156	156

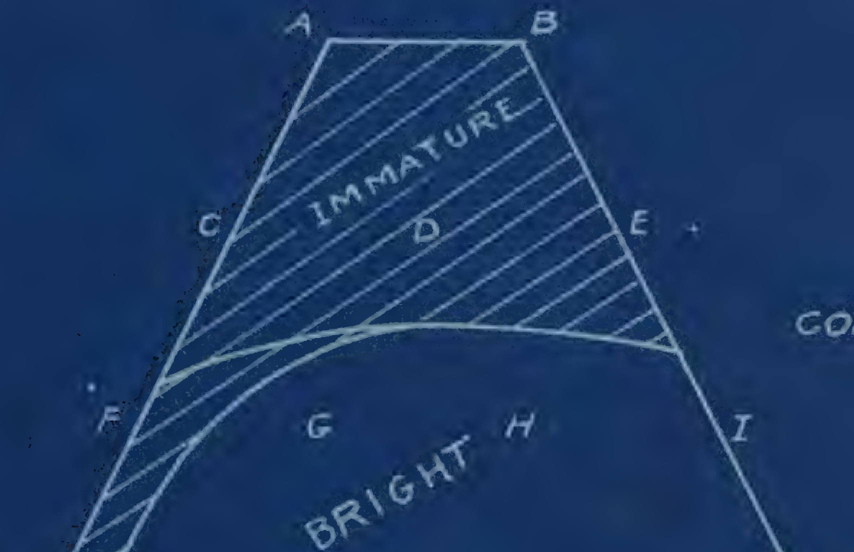
FIGURE III

SERIES I



CONE 9

Shaded Areas Represent Crazing



CONE 10

The glazes were burned in wadded saggers, which had been washed with a mixture of the glazes used, in a down draft kiln in forty hours. The temperature was raised at the rate of fifty degrees an hour up to 1000 degrees and from then on fifteen degrees per hour. Cone ten was soaked down in about four hours.

Two preliminary burns were made of series I and II in order to determine the cone temperature at which the greatest number of these glazes matured. The first burn which was made in a gas fired kiln and lasted thirty-six hours at cone eleven was found to be too high, all of the glazes having a bubbled appearance and wavy surfaces. Thus no distinction could be drawn between the several glazes since all were burned too high.

The second burn was made at cone nine. By comparing this burn with the one at cone eleven it was determined that cone nine was not sufficiently high enough to mature the glazes properly, as they lacked gloss and smoothness of texture. The results of this second burn are as follows:

CONE NINE BURN

SERIES I

Glazes A and B were both immature, glaze B also being crazed. Glaze C was immature and had crazed, although a higher burn would probably have made it bright. Glaze D and E were of a shiny greasy texture and were also crazed.

Glaze F was a matte, but was a little underfired, also being crazed. Glaze G was a dull matte and crazed. Glaze H had an egg-shell texture and was crazed. Glaze I was very finely beaded with

a crystal-like appearance. Glaze J, although having a fair glass, had an egg-shell texture and was crazed badly.

Glaze K was the best glaze in series I with good glass and smooth texture. Glazes L and M had fair glass but an egg-shell texture. Glaze N was a matte with rough texture and dull glass.

CONE TEN BURN

SERIES I

This burn was also made in a gas-fired kiln and lasted about forty hours. The results of this burn are shown on Figure III.

Glazes A and B were immature and it is doubtful if a higher burn would have corrected this defect. Glaze C was a dull greasy finish and had crazed badly. Glaze D was a matte and had also crazed. Glaze E had a dull finish seemingly due to minute pin-holes.

Glaze F was a good matte and was crazed. Glaze G had fair gloss and smooth texture; this was one of the best glazes in this series. Glaze H had a fair gloss but slightly rough texture. Glaze I was a matte with egg-shell texture. Glaze J had a smooth surface and bright gloss but was crazed. Glazes K, L, M and N had fair glass but egg-shell textures.

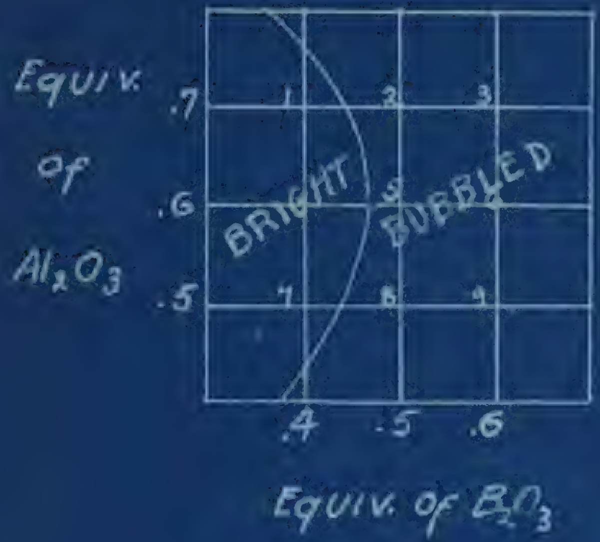
CONE NINE BURN

SERIES II

Glaze A had fair glass but poor opacity and was slightly pin-holed. Glaze B was bubbled and slightly immature. Glaze C although having fair glass was bubbled. Glazes D and E had poor opacity and were bubbled. Glazes F and G had very rough surfaces due to excessive bubbling. Glaze H had egg-shell texture but good gloss. Glaze

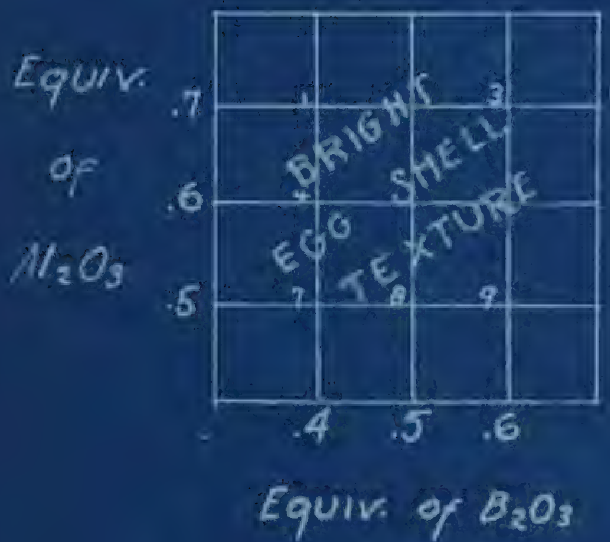
FIGURE IV

SERIES 3



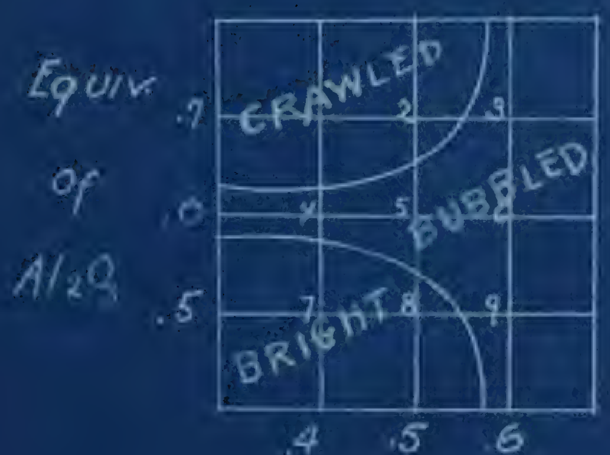
K - RO Group

0.30 K_2O	x Al_2O_3
0.60 CaO	Y B_2O_3
0.10 ZnO	6.0 SiO_2



L - RO Group

0.30 K_2O	x Al_2O_3
0.50 CaO	Y B_2O_3
0.20 ZnO	6.0 SiO_2



M - RO Group

0.30 K_2O	x Al_2O_3
0.40 CaO	Y B_2O_3
0.30 ZnO	6.0 SiO_2

I had a very rough surface, showing a higher burn was necessary to mature it properly. Glaze J was the best glaze in this series although the surface was slightly rough due to egg-shell texture. Glazes K, L, M and N were too viscous and although having fair glass showed an egg-shell texture.

CONE TEN BURN

SERIES II

Glaze A was a white viscous glaze with an egg-shell texture. Glaze B was bubbled badly and was a greenish colored matte. Glazes C and D were dull due to minute pin-holes, although they had fair opacity. Glazes E and F had good gloss but were pin-holed.

Glaze G was badly bubbled and its surface was very rough. Glaze H had a fair gloss but was of a greenish hue. Glaze I was pin-holed with a rough surface. Glaze J was too viscous and was also bubbled. Glaze K had a dull luster due to egg-shell texture. Glaze L was pin-holed and was too viscous. Glazes M and N were beaded and were of a pale greenish color.

This series was peculiar in that there was no crazing while in series I which contained no boric oxide, crazing was prevalent.

SERIES III

In this series the RO groups of glazes K, L, and M from series I and II are kept constant, as is also the silica at six equivalents. The Al_2O_3 and B_2O_3 are varied as shown in Figure IV.

The results of this series are shown on Figure IV. The glazes are numbered in the following manner; for example glaze K-I is the

glaze with the same RO group as glaze K in series I and II and the number I is the number of the glaze as shown on Figure IV.

Glaze K - I although having fair glôss and opacity was badly pin-holed. Thâck application shows a white color and very good opacity. Glazes K-2 and K-3 were of a pale greenish color and were bubbled badly. Glaze K-4 had good gloss and fair opacity but a rough surface. Glazes K-5 and K-6 although having good gloss were bubbled, and when applied thickly showed crawling. Glaze K-7 had good opacity but was opalescent. Glaze K-8 was bubbled and was of a greenish color. Glaze K-9 showed good gloss but very little opacity.

This group was numbered in the same manner as the above group, i.e., L-I glaze is the glaze with the RO group the same as glaze L in series I and II and number 1 is the number as shown on Figure IV.

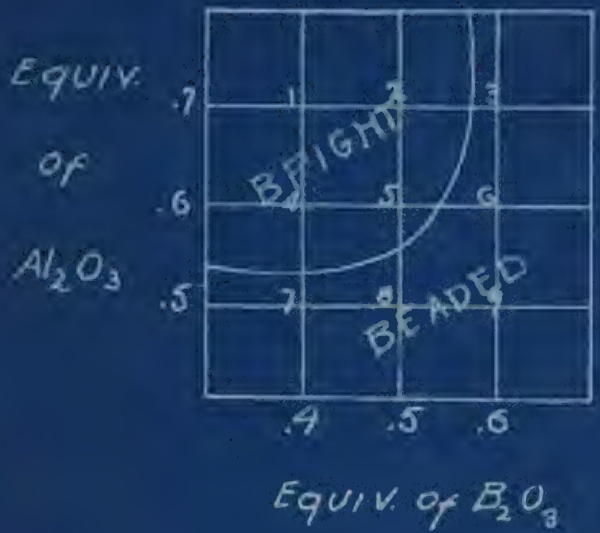
Glaze L-1 was a glossy glaze but had an egg-shell texture. Glazes L-2 and L-3 had very rough surfaces and appeared as if a higher burn was needed to make them glassy glazes. Glazes L-4, L-5 and L-6 although having good gl@ss were of a pale greenish color and had egg-shell textures. Glazes L-7, L-8 and L-9 were mattes and were badly bubbled.

In group M the same nomenclature was used as in the above groups. Glaze M-I and M-2 although having good gloss were badly bubbled. The thick applications of these glazes were a yellowish tinge. Glaze M-4 was a matte with an egg-shell texture.

Glazes M-5 and M-6 were also mattes and showed an egg-shell texture. Glaze M-7 had good opacity but an egg-shell texture. Glaze M-8 had good gloss and good opacity but an egg-shell texture. Glaze M-9 was badly bubbled and very rough, probably due to insufficient temperature.

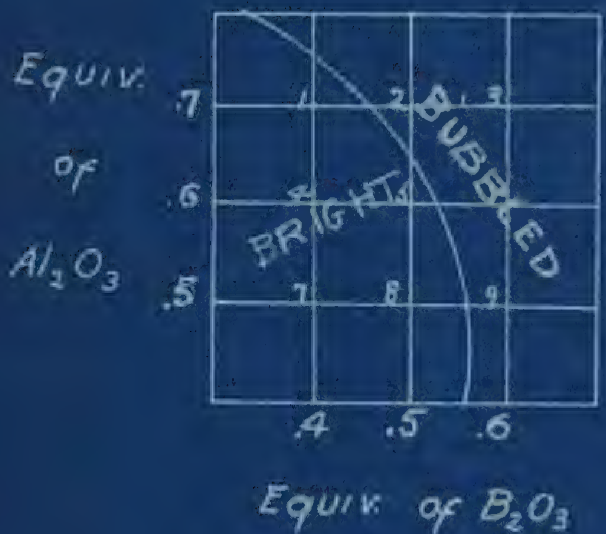
FIGURE V

SERIES - 4



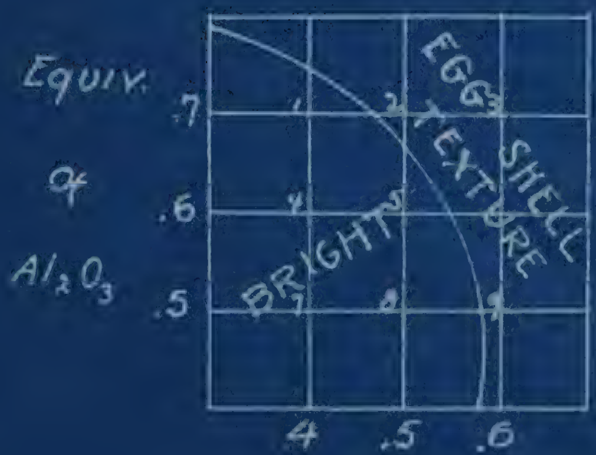
K - RO Group

0.30 K_2O	x Al_2O_3
0.60 CaO	Y B_2O_3
0.10 ZnO	7.0 SiO_2



L - RO - Group

0.30 K_2O	x Al_2O_3
0.50 CaO	Y B_2O_3
0.20 ZnO	7.0 SiO_2



M - RO Group

0.30 K_2O	x Al_2O_3
0.40 CaO	Y B_2O_3
0.30 ZnO	7.0 SiO_2

SERIES IV

The glazes in this series were numbered in the same manner as in series III. This series differs only in that the silica is kept constant at seven equivalents instead of six equivalents as in series III.

Glaze K-1 had very good opacity and good gloss but the surface was covered with minute pin-holes. The glaze was a dull white color. Glaze K-2 showed good gloss but was a greenish color and was bubbled. Glaze K-3 had crawled badly and appeared to be under-fired. Glaze K-4 was one of the best in this series. It had good opacity and gloss but was pin-holed slightly. Glaze K-5 was too viscous and was a greenish color. Glaze K-6 was also too viscous but had a fair gloss. Glaze K-7 showed fair opacity but was a matte due to minute pin-holes on the surface of the glaze. Glaze K-8 had a very good gloss but was too viscous and was a greenish color. Glaze K-9 had crawled badly.

Glaze L-1 was opalescent, also showing bubbling. Glaze L-2 had a good gloss but had an egg-shell texture. Glaze L-3 was too viscous and showed bubbling. Glaze L-4 had fair opacity and good gloss but had an egg-shell surface. Glazes L-5 and L-6 were bubbled badly and were a dirty green color. Glaze L-7 had good opacity but a dull gloss due to pin-holes in the surface. Glaze L-8 was the best glaze in this series; it had fair opacity and a smooth texture but was a greenish color.

Glaze M-1 had good gloss, fair opacity and smooth texture, but was a green color. Glaze M-2 had fair gloss but was bubbled and a greenish color. Glaze M-3 was badly pin-holed but had fair gloss. Glaze M-4 had a good gloss and fair opacity but the surface was

slightly pin-holed.

Glaze M-5 was a white color with good opacity but was bubbled badly. Glaze M-6 was also bubbled but had fair opacity and gloss. Glaze M-7 had very poor opacity and gloss due to pin-holes in surface. Glazes M-8 and M-9 were too viscous and were bubbled and were a greenish color.

In the series containing boric oxide, i.e. series II, III and IV there was no crazing.

CONCLUSIONS

From the results given the following conclusions may be drawn:

1. The effect of the Al_2O_3 as would be expected was to increase the viscosity of the glazes. This was shown by the glazes with high Al_2O_3 content crawling badly. Above 0.50 equivalents, the Al_2O_3 imparted a greenish hue to the glazes.

2. The effect of the B_2O_3 was to decrease the viscosity of the glazes also causing bubbling. The boric oxide also imparted a better gloss to the glazes. Since the series containing no boric oxide crazed and the series with boric oxide did not craze, it may be assumed that B_2O_3 counteracts crazing.

3. The effect of the silica was to raise the viscosity of the glaze slightly. In series IV with seven equivalents of silica, glazes K-6, K-7, K-8 and K-9 showed crawling badly while in series III with only six equivalents of silica there was no evidence of crawling.

4. Above 0.40 equivalents the K_2O caused immaturity and mattes.

5. The effect of the zinc oxide was not as pronounced as one would expect but above 0.30 equivalents it caused beading.

6. None of the glazes attacked the body.

7. Crazing occurred in glazes containing over 0.60 equivalents of CaO and 0.50 equivalents of K_2O. Crazing seemingly may be eliminated by the addition of boric oxide.

BEST GLAZES IN FIELD COVERED

At Cone 10

Glaze H - Series II

0.40 - K_2O	0.60 Al_2O_3
0.40 - CaO	
0.20 - ZnO	6.00 SiO_2

Glaze I - Series I

0.40 - K_2O	0.60 Al_2O_3
0.30 - CaO	
0.30 - ZnO	6.00 SiO_2

Glaze K - Series I

0.30 - K_2O	0.60 Al_2O_3
0.60 - CaO	
0.10 - ZnO	6.00 SiO_2

Glaze L - Series I

0.30 - K_2O	0.60 Al_2O_3
0.50 - CaO	
0.20 - ZnO	6.00 SiO_2

Glaze M - Series I

0.30 - K_2O	0.60 Al_2O_3
0.40 - CaO	
0.30 - ZnO	6.00 SiO_2

Glaze K-I - Series III

0.30 - K_2O	0.70 Al_2O_3
0.60 - CaO	0.40 B_2O_3
0.10 - ZnO	6.00 SiO_2

Glaze M-4 - Series III

0.30 - K_2O	0.60 Al_2O_3
0.40 - CaO	0.40 B_2O_3
0.30 - ZnO	6.00 SiO_2

Glaze M-7 - Series III

0.30 - K_2O	0.50 Al_2O_3
0.40 - CaO	0.40 B_2O_3
0.30 - ZnO	6.00 SiO_2

Glaze K-I - Series IV

0.30 - K_2O	0.70 Al_2O_3
0.60 - CaO	0.40 B_2O_3
0.10 - ZnO	7.00 SiO_2

Glaze K-4 - Series IV

0.30 - K_2O	0.60 Al_2O_3
0.60 - CaO	0.40 B_2O_3
0.10 - ZnO	7.00 SiO_2

Glaze K-7 - Series IV

0.30 - K_2O	0.50 Al_2O_3
0.60 - CaO	0.40 B_2O_3
0.10 - ZnO	7.00 SiO_2

Glaze L-4 - Series IV

0.30 - K_2O	0.60 Al_2O
0.50 - CaO	0.40 B_2O_3
0.20 - ZnO	7.00 SiO_2

Glaze L-7 - Series IV

0.30 - K_2O	0.50 Al_2O_3
0.50 - CaO	0.40 B_2O_3
0.20 - ZnO	7.00 SiO_2

Glaze M-I - Series IV

0.30 - K_2O	0.70 Al_2O_3
0.40 - CaO	0.40 B_2O_3
0.30 - ZnO	7.00 SiO_2

Glaze M-2 - Series IV.

$0.30\ K_2O$ $0.70\ Al_2O_3$
$0.40\ CaO$ $0.50\ B_2O_3$
$0.30\ ZnO$ $7.00\ SiO_2$

Glaze M-3 - Series IV.

$0.30\ K_2O$ $0.70\ Al_2O_3$
$0.40\ CaO$ $0.60\ B_2O_3$
$0.30\ ZnO$ $7.00\ SiO_2$

Glaze M-4 - Series IV.

$0.30\ K_2O$ $0.60\ Al_2O_3$
$0.40\ CaO$ $0.40\ B_2O_3$
$0.30\ ZnO$ $7.00\ SiO_2$

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